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Reactive oxygen species dependent degradation pathway of 4-chlorophenol with Fe@Fe_2O_3 core–shell nanowires

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ABSTRACT

In this study, an environmentally benign polyaminocarboxylic ligand diethylenetriamine pentacetate (DTPA) was first used to promote the aerobic 4-chlorophenol (4-CP) degradation with Fe@Fe_2O_3 core–shell nanowires, and then compared with the most used counterpart ethylenediamine tetraacetate (EDTA) of poor biodegradability. Although the 4-CP removal rate in the Fe@Fe_2O_3/DTPA/Air system was slower owing to the preferential degradation of DTPA, the total organic carbon removal rate in the Fe@Fe_2O_3/DTPA/4-CP/Air system was much faster than that in the Fe@Fe_2O_3/EDTA/4-CP/Air system. We interestingly found that hydroxyl radicals could more easily react with DTPA to produce DTPA radicals than with EDTA to produce EDTA radicals. Ligands (DTPA or EDTA) could significantly accelerate the hydroxyl radicals production with Fe@Fe_2O_3, while more hydroxyl radicals were generated in the Fe@Fe_2O_3/DTPA/Air system. We also employed gas chromatography-mass spectrometry and ion chromatography to detect organic intermediates and chloride ions to probe the 4-chlorophenol degradation pathways, and found its degradation pathways were dependent on the reactive oxygen species generated in the different systems. This study can clarify the roles of polyaminocarboxylic ligands on the molecular oxygen activation with nanoscale zero-valent iron, and also provide a green chlorophenols removal method.

1. Introduction

Chlorophenols are classified as the hazardous and top priority pollutants by the United States Environmental Protection Agency [1,2]. They are chemical intermediates or byproducts in various synthetic industries, and can also be generated during drinking water disinfection process [3,4]. For example, 4-chlorophenol (4-CP) has been widely used in the synthesis of pesticides, herbicides, disinfectants, and wood preservatives. They are irritant to the respiratory and central nervous systems at low levels, and can induce cancer at higher doses. Because of their high toxicity, poor biodegradability, and carcinogenic potential, the removal of chlorophenols is of great significance for environmental protection [5,6].

Advanced oxidation processes (AOPs) could effectively degrade and mineralize chlorophenols via generating highly reactive hydroxyl radicals [7]. However, most of AOPs require the utilization of costly oxidants (ozone and hydrogen peroxide, etc) and/or intense energy (e.g. ultraviolet light and electricity) [7]. Comparing with ozone and hydrogen peroxide, molecular oxygen is a greener and lower cost oxidant ubiquitously existed in the environment. Unfortunately, the reactions between molecular oxygen and chlorophenols are spin-forbidden at ambient conditions. Therefore, it is a challenge to degrade chlorophenols with activated molecular oxygen.

Iron is the fourth most abundant element in the Earth's crust and therefore involved in many important environmental and biochemical processes, including the generation and consumption of reactive oxygen species (ROS), the decomposition and conversion of organics, as well as the respiration and nutrition intake of some microorganism, and so on. Although the generation of ROS via the reaction of zero-valent iron (ZVI) and molecular oxygen has been reported for many years, the application of iron/oxygen chemistry for environmental pollutant control and remediation is far from satisfactory because of its low ROS generation efficiency. The development of nanotechnology provides a solution to solve this low efficiency problem as scientists have found that the utilization of nanoscale zero-valent iron (nZVI) could enhance the ROS generation to some degree [8]. Fe@Fe_2O_3 core–shell nanowires are a special kind of air stable and highly active nZVI developed by our

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group [9]. Very recently, we found Fe@Fe_2O_3 nanowires showed interesting core–shell structure dependent reactivity on the aerobic 4-CP degradation. However, only 77.8% of 4-CP (1.1 mmol/L) could be aerobically degraded with the most reactive Fe@Fe_2O_3 nanowires in 7 h, accompanying with 30% of mineralization in 10 h. Obviously, further efforts must be made to improve the ROS generation by iron/oxygen chemistry for its practical applications.

It is an important breakthrough for scientists to find that ethylenediamine tetraacetate (EDTA), one of polyaminocarboxylic ligands, could significantly improve the generation of ROS via the reaction of ZVI and molecular oxygen for the degradation of various organic pollutants [10]. Nevertheless, EDTA may cause some unfavorable environmental consequences because of its poor biodegradability and superior heavy metal chelating ability. For example, EDTA may form stable water-soluble complexes with many radionuclides to increase the risk of radionuclide transport in the subsurface environment [11]. It is indispensable to find some safe and environmentally benign replacement for EDTA for the environmental control and remediation purposes. In comparison with EDTA, diethylenetriamine pentaacetate (DTPA) ligand is more environmentally friendly [12–14], but much less been paid attention. In this study, we compare the performances of DTPA and EDTA on the aerobic 4-CP degradation with Fe@Fe_2O_3 nanowires by investigating the generation of ROS as well as the degradation and mineralization of 4-CP systematically. The purposes of this study are to clarify the roles of polyaminocarboxylic ligands on the molecular oxygen activation over nZVI and develop a green method to remove chlorophenols.

2. Experimental

2.1. Chemicals and materials

DTPA, $FeCl_3{\cdot}6H_2O$, $NaBH_4$, TA, and 1,10-phenanthroline monohydrate were all of commercially available analytical grade and purchased from National Medicines Corporation Ltd. of China. 4-CP was purchased from Acros. Superoxide dismutase (SOD), horseradish peroxidase, and *p*-hydroxyphenylacetic acid (POHPAA) were purchased from Aladdin. CH_3OH, C_2H_5OH, C_3H_7OH, and C_4H_9OH were purchased from National Medicines Corporation Ltd. of China. High performance liquid chromatography (HPLC) grade acetonitrile were obtained from Merck. All the chemicals were used as received without further purification. Fe@Fe_2O_3 core–shell nanowires were synthesized by the reaction between ferric chloride and sodium borohydride described previously [15]. Deionized water was used in all experiments.

2.2. Experimental procedure

The aerobic 4-CP degradation experiments were carried out at room temperature ($20 \pm 2\,^{\circ}C$). 4-CP and diethylenetriaminepentacetic acid were dissolved in aqueous solution. The initial pH of 4-CP and diethylenetriaminepentacetic acid solution was 2.7. To obtain the same initial pH, the pH of 4-CP and ethylenediamine tetraacetate disodium salt solution was adjusted to 2.7 with 1 mol/L HCl solution. In a typical degradation, Fe@Fe_2O_3 nanowires were added into 4-CP (1.1 mmol/L) and ligand (2 mmol/L) solution with an initial concentration of 0.1 g/L. Air or argon was bubbled into the solution at a rate of 1.5 L/min to continuously supply molecular oxygen or remove molecular oxygen, respectively. During the degradation, the solution samples were taken out from the flask with a syringe at predetermined time intervals and filtered immediately through a 0.22-μm microporous membrane (mixed cellulose esters membrane) for analysis. For comparison, the aerobic 4-CP degradation experiment with 0.1 g/L of Fe@Fe_2O_3 nanowires in the absence of any polyaminocarboxylic ligand was conducted after adjusting the initial pH of the 4-CP solution to 2.7. The self degradation of 4-CP under air atmosphere and the 4-CP degradation with Fe@Fe_2O_3 and DTPA in argon or oxygen atmosphere were also conducted for comparison.

2.3. Analytic methods

Total organic carbon (TOC) analysis was performed on a TOC analyzer (TOC-V_{CPH}, Shimadzu, Japan) after filtration through 0.22-μm microporous membrane. Methanol, isopropanol, and ethanol were used to probe the generation of •OH in the bulk solution ($\bullet OH_{sol}$), total hydroxyl radical ($\bullet OH_{total}$), as well as both •OH and ferryl ions, respectively [8]. Terephthalic acid (TA) was employed as the fluorescent probe for the detection of hydroxyl radicals. 2-hydroxyterephthalic acid (TAOH), which is the fluorescent product of the reaction of TA with •OH, has a strong fluorescent emission at around 426 nm when excited at 312 nm [16]. Electron spin resonance (ESR) spectra were obtained with a Bruker A300 ESR spectrometer with employing 5,5-dimethyl-L-pyrroline-*N*-oxide (DMPO) as the spin trapper at room temperature. Fifty microliter aliquots of control or sample solutions were put into glass capillary tubes with internal diameters of 1 mm and then sealed. The capillary tubes were inserted into the ESR cavity, and the spectra were recorded at selected times. The dissolved ferrous ions was quantified with the 1, 10-phenanthrolin method [17]. Samples were analyzed by a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan) at maximum wavelength of 510 nm. Hydrogen peroxide (H_2O_2) was measured by using the horseradish peroxidase-mediated dimerization of POHPAA [18]. The chloride ions and small molecule acids were monitored by an ion chromatographer (Dionex ICS900, Thermo, USA) equipped with IonPac AS14A Anion-Exchange Column. The mobile phase was composed of 8.0 mmol/L Na_2CO_3 and 1.0 mmol/L $NaHCO_3$. Samples were analyzed at a flow rate of 1 mL/min. The 4-CP concentration was analyzed by high performance liquid chromatography (HPLC, LC-20A, Shimadzu, Japan) with an Agilent TC-C18 reverse phase column (4.6 × 150 mm, 5 μm) and ultraviolet detector setting at the wavelength of 279 nm. The mobile phase was a mixture of acetonitrile and water with 1:1 volume ratio. The injection volume was 10 μL. Samples were analyzed at a flow rate of 0.5 mL/min. The intermediates were analyzed by a gas chromatography-mass spectrometer (GC–MS, Trace 1300-ISQ, Thermo, USA) with Agilent DB-17 capillary column (30 m × 0.25 mm × 0.50 μm). The temperature of the injection block was 300 °C; the oven temperature program was 60 °C, rising at 10 °C/min to a final temperature of 280 °C. Helium was used as the carrier gas at the flow rate of 1 mL/min.

3. Results and discussion

3.1. The removal of 4-CP and TOC

4-CP could not be degraded with air in the absence of Fe@Fe_2O_3, while DTPA or EDTA did not induce the aerobic 4-CP degradation alone. Only 22.3% of 4-CP was aerobically degraded with Fe@Fe_2O_3 in 2 h. The 4-CP removal efficiencies in 2 h reached 100% and 97.3% for the Fe@Fe_2O_3/EDTA/Air and Fe@Fe_2O_3/DTPA/Air systems, respectively (Fig. 1a). The aerobic 4-CP degradation processes were found to follow pseudo-first order kinetics within 90 min (Fig. 1b), while the 4-CP degradation rate constants were 0.0036, 0.0244, and 0.0682 min^{-1} for the Fe@Fe_2O_3/Air, Fe@Fe_2O_3/DTPA/Air and Fe@Fe_2O_3/EDTA/Air systems, respectively. As expected, the addition of polyaminocarboxylic ligands (EDTA or DTPA) could greatly enhance the aerobic 4-CP degradation with Fe@Fe_2O_3, and the

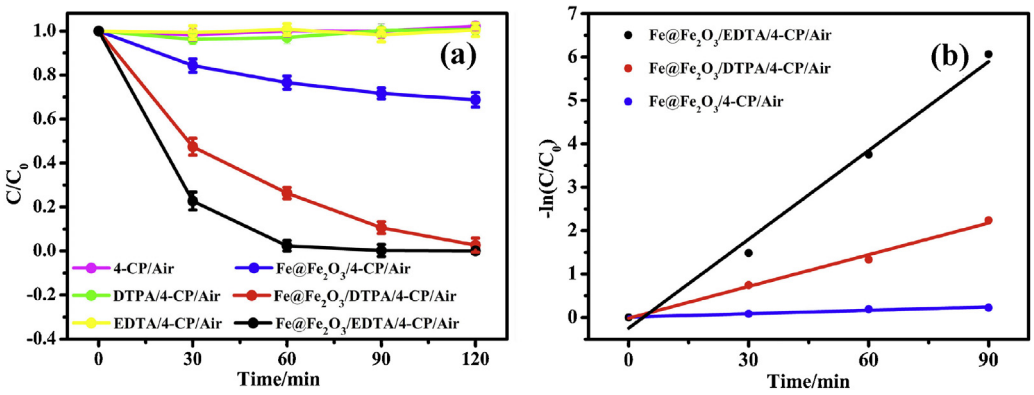


Fig. 1. (a) The temporal concentration changes of 4-CP as a function of time in the 4-CP/Air, DTPA/4-CP/Air, ETDA/4-CP/Air, $Fe@Fe_2O_3$/4-CP/Air, $Fe@Fe_2O_3$/DTPA/4-CP/Air, and $Fe@Fe_2O_3$/EDTA/4-CP/Air systems; (b) plots of $-\ln(C/C_0)$ versus time.

aerobic 4-CP degradation rate in the $Fe@Fe_2O_3$/EDTA/Air system was nearly 2.8 times that in the $Fe@Fe_2O_3$/DTPA/Air system within 90 min. However, the TOC removal rate in the $Fe@Fe_2O_3$/DTPA/4-CP/Air system was 2.4 times that in the $Fe@Fe_2O_3$/EDTA/4-CP/Air system (Fig. 2a). As both the organic ligands and 4-CP contributed to the TOC values of $Fe@Fe_2O_3$/ligand/4-CP/Air systems, we therefore monitored the TOC changes in the $Fe@Fe_2O_3$/DTPA/Air and $Fe@Fe_2O_3$/EDTA/Air systems without adding 4-CP and found 64.1% of TOC was removed in the $Fe@Fe_2O_3$/DTPA/Air system within 1 h. This value was much higher than the TOC removal percentage (< 30%) in the $Fe@Fe_2O_3$/EDTA/Air system (Fig. 2b). Obviously, the 4-CP concentration changes in the $Fe@Fe_2O_3$/DTPA/4-CP/Air and $Fe@Fe_2O_3$/EDTA/4-CP/Air systems were different from the TOC changes. To understand this difference, we further monitored the concentration variation of released chloride ions during the aerobic 4-CP degradation. The dechlorination efficiencies of the $Fe@Fe_2O_3$/4-CP/Air, $Fe@Fe_2O_3$/DTPA/4-CP/Air and $Fe@Fe_2O_3$/EDTA/4-CP/Air systems were 29.8%, 92.5% and 94.1% in 2 h, respectively (Fig. 2c), suggesting that the two ligands (DTPA or EDTA) could significantly enhance the aerobic 4-CP dechlorination with Fe@Fe2O3. Therefore, the $Fe@Fe_2O_3$/DTPA/Air system exhibited lower 4-CP degradation and dechlorination efficiencies than the $Fe@Fe_2O_3$/EDTA/Air counterpart, but higher TOC removal efficiency. We attributed this inconsistency to the preferential degradation and the faster mineralization rate of DTPA during the simultaneous 4-CP and ligand removal processes.

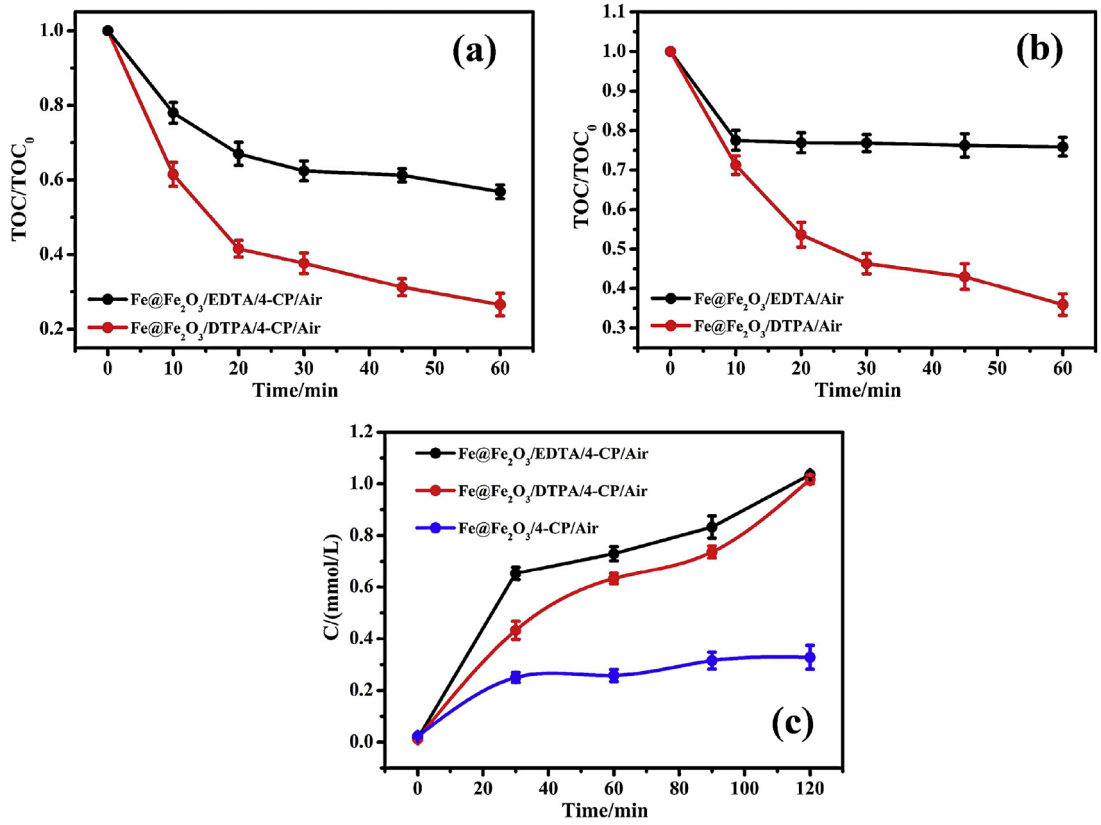


Fig. 2. (a) Normalized TOC changes as a function of time in the $Fe@Fe_2O_3$/EDTA/4-CP/Air and $Fe@Fe_2O_3$/DTPA/4-CP/Air systems; (b) normalized TOC changes as a function of time in the $Fe@Fe_2O_3$/EDTA/Air and $Fe@Fe_2O_3$/DTPA/Air systems; (c) the concentration variation of chloride ions released during the 4-CP degradation process in the $Fe@Fe_2O_3$/4-CP/Air, $Fe@Fe_2O_3$/DTPA/4-CP/Air and $Fe@Fe_2O_3$/EDTA/4-CP/Air systems.

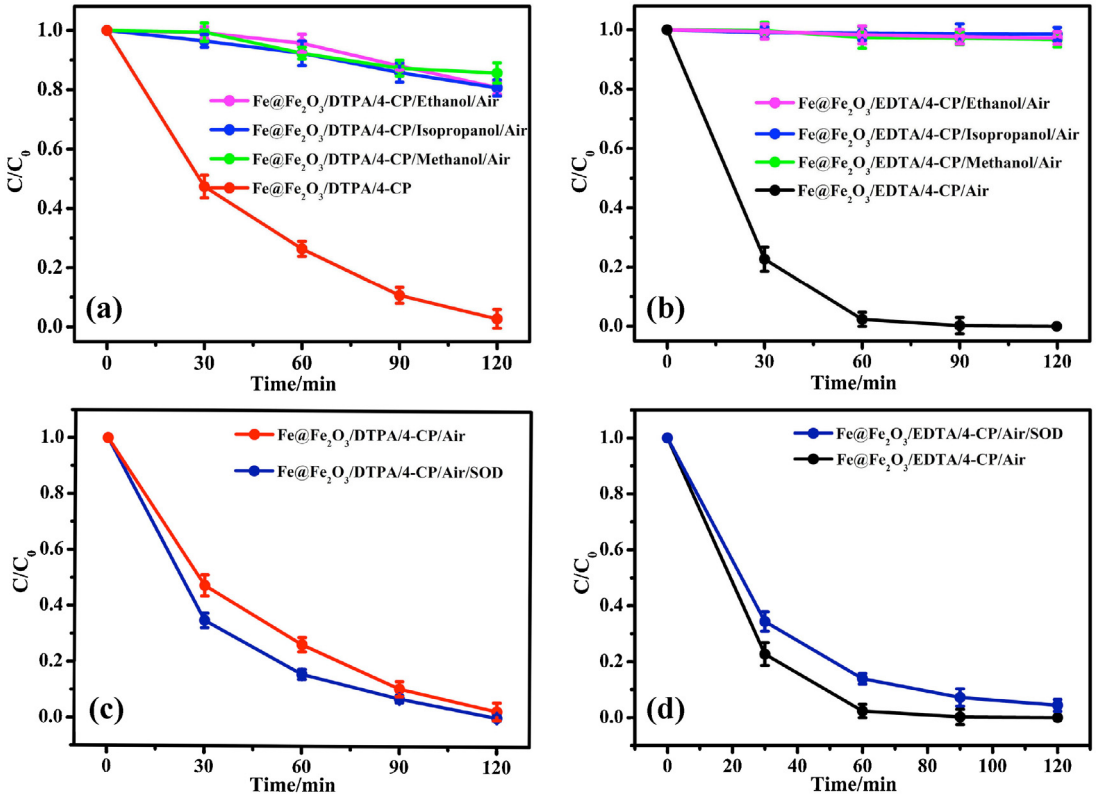


Fig. 3. Degradation of 4-CP in the presence of ethanol, isopropanol, and methanol: (a) the Fe@Fe_2O_3/DTPA/4-CP/Air system; (b) the Fe@Fe_2O_3/EDTA/4-CP/Air system; degradation of 4-CP in the presence of SOD; (c) the Fe@Fe_2O_3/DTPA/4-CP/Air system; (d) the Fe@Fe_2O_3/EDTA/4-CP/Air system.

3.2. The generation and roles of radicals

To clarify the simultaneous 4-CP and ligand removal in the Fe@Fe_2O_3/DTPA/4-CP/Air and Fe@Fe_2O_3/EDTA/4-CP/Air systems, we first analyzed the production of ROS in these two systems with adding different scavengers (ethanol for both •OH and the ferryl ion, isopropanol for total •OH, methanol for •OH in the bulk solution, SOD for $•O_2^-$). As shown in Fig. 3a and b, the addition of ethanol or isopropanol could largely inhibit the aerobic 4-CP degradation in the two systems with similar inhibition effects. This revealed the major oxidative species for the 4-CP degradation in these two systems were •OH. We also found that the aerobic 4-CP degradation was remarkably inhibited by methanol and therefore concluded that the 4-CP degradation in the two systems was mainly attributed to the •OH in the bulk solution ($•OH_{sol}$). These $•OH_{sol}$ are thought to be generated by the reaction between diffusing H_2O_2 and Fe(II) (or [Fe(II)-ligand (DTPA or EDTA)]) [19]. Interestingly, we found that $•O_2^-$ played different roles in these two systems, as the 4-CP degradation efficiency increased after the addition of SOD in the Fe@Fe_2O_3/DTPA/4-CP/Air system (Fig. 3c), but decreased in the case of Fe@Fe_2O_3/EDTA/4-CP/Air (Fig. 3d). The SOD induced 4-CP degradation efficiency decrease suggested that $•O_2^-$ might directly contribute to the reductive dechlorination of 4-CP in the Fe@Fe_2O_3/EDTA/4-CP/Air system [9]. We thought that this promotion effect of SOD on the 4-CP degradation efficiency in the Fe@Fe_2O_3/DTPA/4-CP/Air system was related to the SOD promoted transformation of $•O_2^-$ into •OH via the $•O_2^- \rightarrow H_2O_2 \rightarrow$ •OH pathway. If $•O_2^-$ did not participate in the 4-CP degradation directly in the Fe@Fe_2O_3/DTPA/4-CP/Air system, its disproportionation into H_2O_2 could be accelerated by SOD [20], resulting in more •OH generation via Fenton reaction for the enhanced 4-CP degradation. We therefore conclude that $•O_2^-$ is directly involved in the reductive dechlorination of 4-CP in the Fe@Fe_2O_3/EDTA/4-CP/Air system, but indirectly contribute to the oxidative degradation of 4-CP in the Fe@Fe_2O_3/DTPA/4-CP/Air system via its further transformation into •OH.

Recently, we found that the ligand-free aerobic 4-CP degradation with Fe@Fe_2O_3 nanowires was co-governed by two molecular oxygen activation pathways, leading to an interesting core–shell structure dependent reactivity of Fe@Fe_2O_3 nanowires [9]. Among two pathways, one was the two-electron reduction of O_2 to generate H_2O_2 by the Fe^0, which was realized through the electron transfer from the Fe^0 core to the surface of iron oxide shell. The other was the one-electron reduction of O_2 to $•O_2^-$ by the surface bound ferrous ions ($\equiv Fe^{III}OFe^{II}OH/\equiv Fe^{II}OFe^{III}OH$). The produced $•O_2^-$ could further react with protons and electrons to produce H_2O_2. All the produced H_2O_2 could then react with the surface bound and dissolved ferrous ions to generate •OH through Fenton reaction. To figure out the roles of ligands (DTPA or EDTA) on the enhanced aerobic 4-CP degradation with Fe@Fe_2O_3 nanowires, we first monitored the concentration variations of Fe(II) in the Fe@Fe_2O_3/Air, Fe@Fe_2O_3/DTPA/Air and Fe@Fe_2O_3/EDTA/Air systems and found that ligands (DTPA or EDTA) could significantly accelerate the release of Fe(II) from iron core of Fe@Fe_2O_3, while more Fe(II) were released in the Fe@Fe_2O_3/DTPA/Air system (Fig. 4). Because the two-electron molecular oxygen reduction process is related with the oxidation of Fe^0 to ferrous ions and the ligands (DTPA or EDTA) can facilitate the oxidation of Fe(II) to Fe(III) [21], contributing to the one-electron reduction of O_2 to $•O_2^-$, we proposed that ligands (DTPA or EDTA) might favor both the two-electron and one-electron molecular oxygen reduction processes, which was confirmed by the enhanced H_2O_2 generation with Fe@Fe_2O_3 nanowires in the presence of ligands (Fig. 5). Meanwhile, we also noticed that more H_2O_2 was generated in

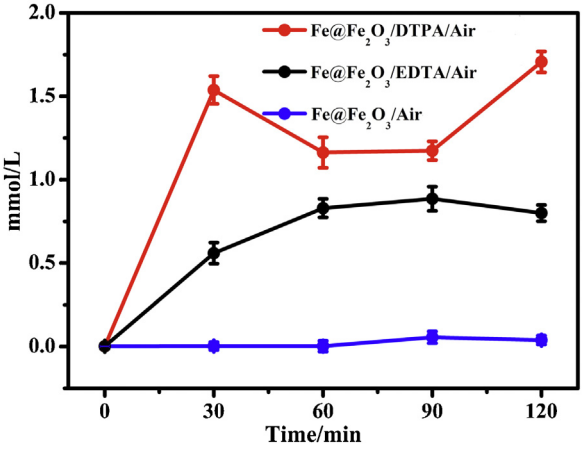


Fig. 4. Comparative concentration of Fe(II) in the Fe@Fe_2O_3/DTPA/Air, Fe@Fe_2O_3/EDTA/Air, and Fe@Fe_2O_3/Air systems.

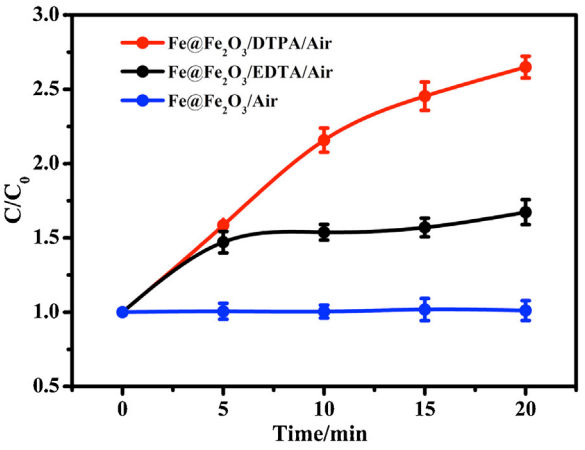


Fig. 5. Comparative production of H_2O_2 in the Fe@Fe_2O_3/DTPA/Air, Fe@Fe_2O_3/EDTA/Air, and Fe@Fe_2O_3/Air systems.

the Fe@Fe_2O_3/DTPA/Air system, suggesting that DTPA was more effective to enhance molecular oxygen activation with Fe@Fe_2O_3 nanowires than EDTA.

It is known that H_2O_2 can react with ferrous ions to produce •OH through Fenton reaction. Spin-trapping ESR technique was therefore employed to identify the short-lived radicals generated in the Fe@Fe_2O_3/EDTA/Air and Fe@Fe_2O_3/DTPA/Air systems. Two major kinds of radicals were observed in the Fe@Fe_2O_3/EDTA/Air system (Fig. 6a). The poor signal with a ratio of about 1:1:1:1 was assigned to DMPO–•OH [22], and the other stronger ESR signal might be arisen from carbon center radicals like DMPO–•CH_2COOH or DMPO–•EDTA [23–25], which could be produced via the reaction between EDTA and •OH [26]. However, only carbon center radical signal was observed in the typical ESR spectrum of Fe@Fe_2O_3/DTPA/Air system (Fig. 6b). The disappearance of DMPO–•OH signal suggested that all the generated •OH was instantly consumed in the Fe@Fe_2O_3/DTPA/Air system because DTPA was easier to react with •OH to produce DTPA radicals (•DTPA) than EDTA [27], consistent with the environmentally benign characteristic of DTPA.

The TA fluorescent probe method was then used to compare the •OH production in the Fe@Fe_2O_3/Air, Fe@Fe_2O_3/EDTA/Air and Fe@Fe_2O_3/DTPA/Air systems. As ligands (DTPA or EDTA) would compete with TA to react with •OH, and the rate constants of ligands and •OH ($k_{(•OH+EDTA)} = 2.8 \times 10^9$ L/mol/s, $k_{(•OH+DTPA)} = 5.2 \times 10^9$ L/mol/s) had the same order of magnitude as that of TA and •OH ($k_{(•OH+TA)} = 4.0 \times 10^9$ L/mol/s) [27–29], we increased the initial concentration of TA to three orders of magnitude that of ligands (DTPA or EDTA) to get desirable fluorescent signal of 2-hydroxyterephthalic acid, which is produced by the reaction of TA with •OH generated in the systems. Although both DTPA and EDTA could significantly enhance the •OH amount generated via Fe@Fe_2O_3 induced molecular oxygen activation, the •OH generation curve of the Fe@Fe_2O_3/DTPA/Air system was significantly different from that of Fe@Fe_2O_3/EDTA/Air. The amount of 2-hydroxyterephthalic acid in the Fe@Fe_2O_3/EDTA/Air system increased linearly within 120 min (Fig. 7a), suggesting its continuous generation of •OH. As for the Fe@Fe_2O_3/DTPA/Air system, it generated much more 2-hydroxyterephthalic acid than the Fe@Fe_2O_3/EDTA/Air system within the first 30 min (Fig. 7a). Surprisingly, the fluorescent intensity of 2-hydroxyterephthalic acid decreased gradually after 30 min (Fig. 7a), revealing the decomposition of 2-hydroxyterephthalic acid in the Fe@Fe_2O_3/DTPA/Air system. This decomposition might be ascribed to too much •OH produced in the presence of DTPA. The excess •OH would destroy 2-hydroxyterephthalic acid generated via the reaction of TA and •OH. Similar phenomena were also observed previously [30,31]. These •OH measurement results revealed that environmentally benign DTPA was more efficient to enhance molecular oxygen activation with Fe@Fe_2O_3 nanowires than EDTA.

Besides the molecular oxygen activation reactions, zero-valent iron can also reduce proton to hydrogen, which is thought be a competitive side reaction of molecular oxygen activation [32]. We therefore investigated the influences of two ligands on the

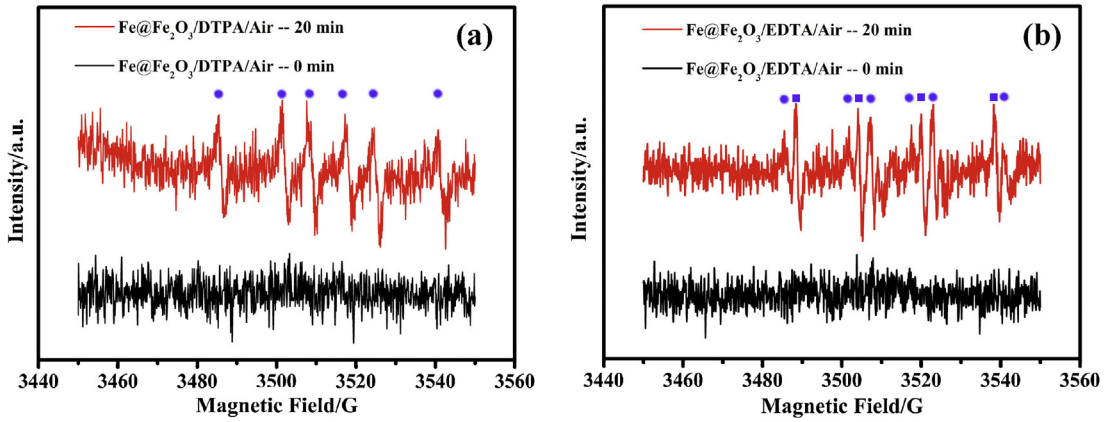


Fig. 6. ESR spectra obtained from samples containing (a) DMPO + Fe@Fe_2O_3 + DTPA; (b) DMPO + Fe@Fe_2O_3 + EDTA at 0 min (black curve) and at 20 min (red curve) under air atmosphere.

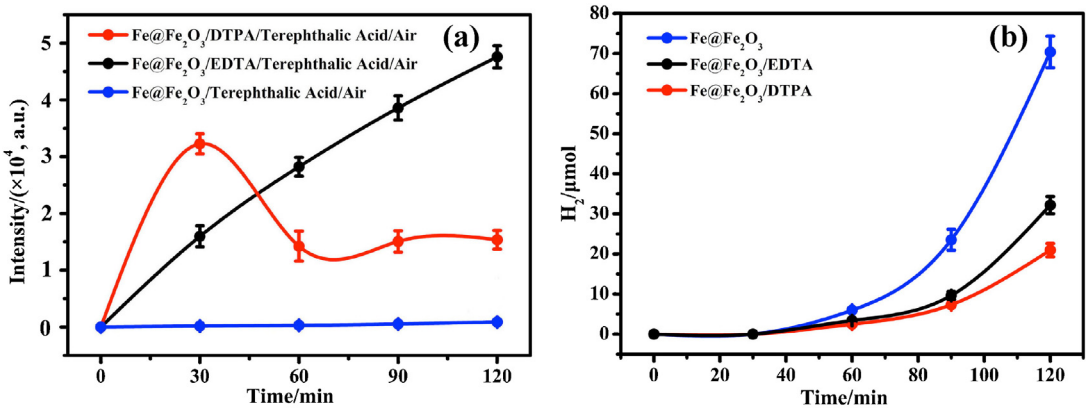


Fig. 7. (a) Time profile of production of 2-hydroxyterephthalic acid in the Fe@Fe_2O_3/Air, Fe@Fe_2O_3/DTPA/Air and Fe@Fe_2O_3/EDTA/Air systems; (b) the temporal production change of H_2 as a function of reaction time.

hydrogen evolution through the reduction of proton by Fe@Fe_2O_3 nanowires. The hydrogen production of the Fe@Fe_2O_3/4-CP/Air, Fe@Fe_2O_3/DTPA/4-CP/Air and Fe@Fe_2O_3/EDTA/4-CP/Air systems were 70.4, 20.9, 32.2 μmol in 2 h, respectively (Fig. 7b). The results revealed that both DTPA and EDTA inhibited the hydrogen evolution over Fe@Fe_2O_3 nanowires, while DTPA exhibited higher inhibition effect. This phenomenon revealed that DTPA could more effectively suppress the hydrogen evolution through the reduction of proton by Fe@Fe_2O_3 to leave behind more electrons from iron core for the molecular oxygen activation and the subsequent 4-CP degradation.

3.3. The reaction intermediates and pathways

GC–MS analysis was further employed to investigate the 4-CP degradation pathways in the Fe@Fe_2O_3/Air, Fe@Fe_2O_3/EDTA/Air, and Fe@Fe_2O_3/DTPA/Air systems. Both oxidative (hydroquinone) and reductive (phenol) intermediates of 4-CP were detected in the Fe@Fe_2O_3/4-CP/Air system. However, only oxidative intermediates were found in the Fe@Fe_2O_3/EDTA/4-CP/Air and Fe@Fe_2O_3/DTPA/4-CP/Air systems (Fig. 8a and b). This difference indicated that the presence of polyaminocarboxylic ligands could promote the oxidative process during the aerobic 4-CP degradation with Fe@Fe_2O_3 nanowires. Besides hydroquinone detected in the Fe@Fe_2O_3/EDTA/4-CP/Air systems (Fig. 8b), other two oxidative intermediates (4-chlorocatechol and 4-chlororesorcinol) were found in the Fe@Fe_2O_3/DTPA/Air/4-CP system (Fig. 8a), suggesting that the oxidative process was further promoted because of more hydroxyl radicals generated in the system. Ion chromatograph analysis results further confirmed the enhanced 4-CP oxidation in the presence of polyaminocarboxylic ligands. The amount of small molecule acids (e.g. CH_3COOH and HCOOH) generated in the two ligand-existed systems was much more than that in the ligand-free system, while the Fe@Fe_2O_3/DTPA/4-CP/Air system had the highest small molecule acids production (Fig. 9). This was consistent with more hydroxyl radicals generated in the Fe@Fe_2O_3/DTPA/4-CP/Air system than in the other two systems. Obviously, the 4-CP degradation pathways were dependent on the generated reactive oxygen species in this study.

On the basis of the results and analyses, we would explain the reactive oxygen species dependent 4-CP degradation pathways in the three systems as follows. In the absence of polyaminocarboxylic ligands, the amount of generated •OH was tiny, $•O_2^-$ induced reductive dechlorination of 4-CP was therefore overwhelming, resulting in the phenol generation in the Fe@Fe_2O_3/4-CP/Air system. The appearance of hydroquinone instead of phenol in the Fe@Fe_2O_3/EDTA/4-CP/Air system reflected the oxidative ability enhancement after adding EDTA. Hydroquinone might be generated in two ways. One was directly via the attack of C—Cl bonds of 4-CP by •OH. The other was indirectly through the further oxidation of phenol (the reductive dechlorination product of 4-CP)

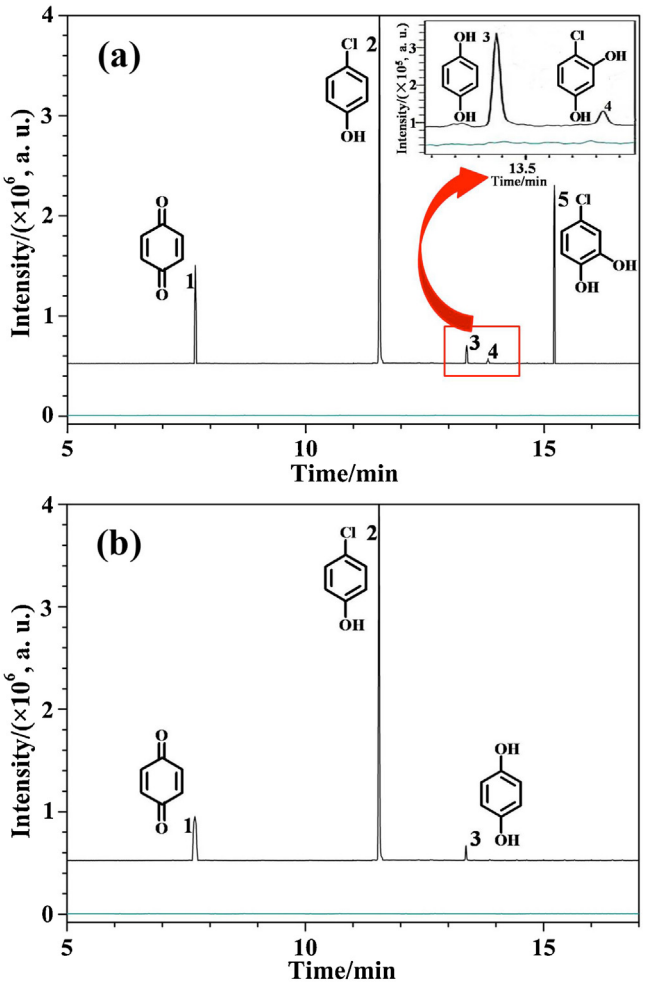


Fig. 8. Typical GC–MS chromatograms for 4-CP degradation: (a) the Fe@Fe_2O_3/DTPA/4-CP/Air system; (b) the Fe@Fe_2O_3/EDTA/4-CP/Air system.

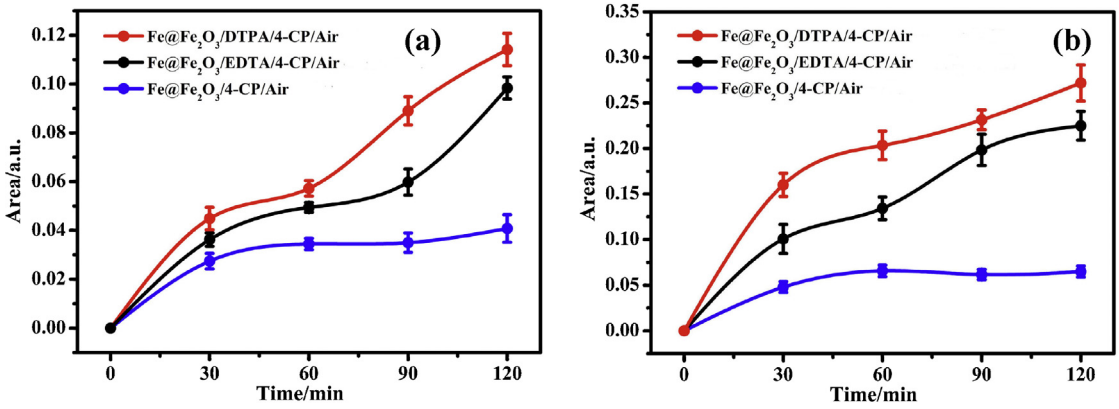
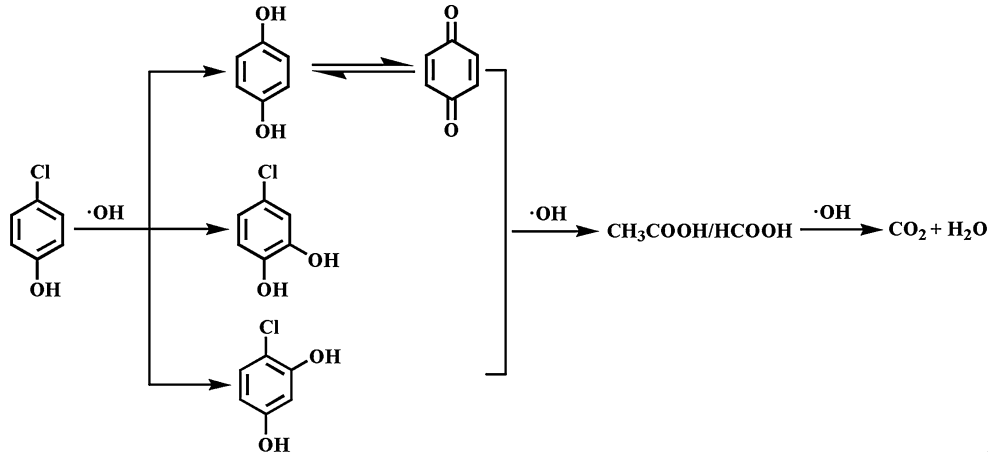
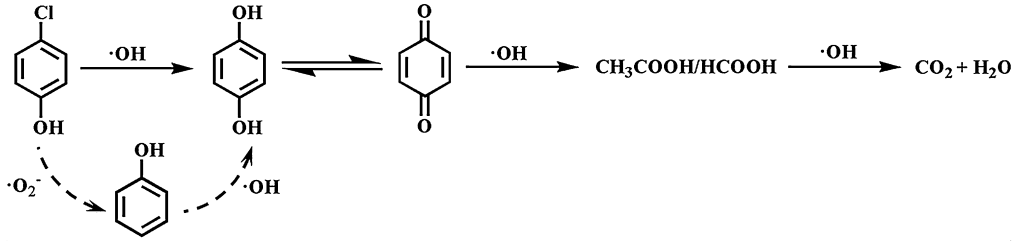


Fig. 9. Comparative production of (a) HCOOH; (b) CH_3COOH in the $Fe@Fe_2O_3$/4-CP/Air, $Fe@Fe_2O_3$/EDTA/4-CP/Air and $Fe@Fe_2O_3$/DTPA/4-CP/Air systems.

(a) In the $Fe@Fe_2O_3$/DTPA/4-CP/Air System:



(b) In the $Fe@Fe_2O_3$/EDTA/4-CP/Air System:



Scheme 1. The possible 4-CP degradation mechanisms: (a) the $Fe@Fe_2O_3$/DTPA/4-CP/Air system; (b) the $Fe@Fe_2O_3$/EDTA/4-CP/Air system.

with •OH produced in the presence of EDTA (Scheme 1a). As for the $Fe@Fe_2O_3$/DTPA/Air/4-CP system, it was highly possible that hydroquinone was formed directly through the attack of C—Cl bonds of 4-CP by •OH. This was because $•O_2^-$ just indirectly contributed to the 4-CP degradation by its transformation into •OH via $•O_2^- \rightarrow H_2O_2 \rightarrow$ •OH in the $Fe@Fe_2O_3$/DTPA/Air/4-CP system, as revealed by the $•O_2^-$-trapping experiment results. The other two oxidative intermediates (4-chlorocatechol and 4-chlororesorcinol) were generated via the attack of C—H bonds of 4-CP by •OH because much more •OH was produced in the $Fe@Fe_2O_3$/DTPA/4-CP/Air system (Scheme 1b). Subsequently, these oxidative and reductive intermediates were further decomposed to small molecule acids (e.g. acetic acid and formic acid), and finally mineralized into CO_2 and H_2O under the co-attack of $•O_2^-$ and •OH.

4. Conclusions

In summary, we have demonstrated that the environmentally friendly diethylenetriamine pentacetate ligand is more effective to promote molecular oxygen activation with $Fe@Fe_2O_3$ core–shell nanowires than the most used ethylenediamine tetraacetate of poor biodegradable property. Both diethylenetriamine pentacetate ligand and 4-chlorophenol could be rapidly mineralized by more hydroxyl radicals generated through $Fe@Fe_2O_3$ nanowires induced molecular oxygen activation in the presence of DTPA. We

interestingly found that hydroxyl radicals could more easily react with DTPA to produce DTPA radicals than with EDTA to produce EDTA radicals. The GC–MS and IC detection results revealed that 4-CP degradation pathways were dependent on the reactive oxygen species generated in the different systems. This study can clarify the roles of polyaminocarboxylic ligands on the molecular oxygen activation with nanoscale zero-valent iron, and also provide a green chlorophenols removal method.

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